



Europäisches Patentamt
European Patent Office
Office européen des brevets



⑪ Veröffentlichungsnummer: **0 639 539 A1**

⑫

EUROPÄISCHE PATENTANMELDUNG

⑰ Anmeldenummer: 94112189.9

⑸ Int. Cl.⁶: C04B 26/06, C08F 2/44,
C08K 3/22, C08K 3/00,
A47K 1/00, A47K 3/00

⑱ Anmeldetag: 04.08.94

⑳ Priorität: 17.08.93 DE 4327610

㉑ Veröffentlichungstag der Anmeldung:
22.02.95 Patentblatt 95/08

㉒ Benannte Vertragsstaaten:
AT BE CH DE DK ES FR GB IT LI NL SE

㉓ Anmelder: RÖHM GMBH
Kirschenallee
D-64293 Darmstadt (DE)

㉔ Erfinder: Krieg, Manfred, Dr.
Kesselhutweg 19
D-64289 Darmstadt (DE)
Erfinder: Ittmann, Günther
Waldstrasse 15
D-64823 Gross-Umstadt (DE)

㉕ Verfahren zur Herstellung gegossener, hochgefüllter Polymethylmethacrylat-Formteile.

㉖ Die Erfindung betrifft ein Verfahren zur Herstellung gefüllter Formteile auf Polymethylmethacrylatbasis mittels Substanzpolymerisation in einer geeigneten Polymerisationskammer, wobei man in an sich bekannter Weise eine flüssige, die Monomeren enthaltende Polymervorstufe PV herstellt, in die unter hochtourigem Rühren unter Bildung einer Suspension SP der partikelförmige Füllstoff FS in Anteilen von 30 bis 80 Gew.-% bezogen auf die gebildete Suspension SP eingetragen wird und wobei man der Suspension SP kurz vor dem Verfüllen in die Polymerisationskammer einen Radikal-Initiator und ein festes, teilchenförmiges Polymerisat PP in Anteilen von 1 bis 20 Gew.-% bezogen auf die Suspension SP in gleichmäßiger Verteilung zusetzt, anschließend in die Polymerisationskammer verfüllt, dann die Polymerisation durchführt und Entformung vornimmt.

EP 0 639 539 A1

Rauch-Puntigam, Th. Völker, "Acryl- und Methacrylverbindungen", Seite 184, Springer-Verlag, 1967), wobei exemplarisch Ethylenglykoldimethacrylat, 1,4-Butandiol dimethacrylat, Triglykoldimethacrylat, Trimethylolpropantrimethacrylat und -acrylat, Allylverbindungen wie Allylmethacrylat oder Triallylcyanurat genannt seien. Der Gehalt an vernetzenden Monomeren liegt im allgemeinen bei 0,1 bis 1,5 Gew.-% bezogen auf die Monomeren. Außer den Monomeren enthält die Polymervorstufe PV vorzugsweise ein Praepolymerisat PM in Anteilen von 1 bis 15 Gew.-% bezogen auf die Polymervorstufe PV.

Als Praepolymerisat PM kommen z.B. die einschlägig verwendeten PMMA-Polymerisate infrage, die gegebenenfalls untergeordnete Anteile, bis etwa 15 Gew.-% an zweckmäßig ausgewählten Comonomeren wie z.B. Methacrylat enthalten können. Die Praepolymerisate haben üblicherweise eine Molmasse im Bereich 2×10^4 bis 4×10^5 Dalton [Bestimmung durch Size Exclusion Chromatography (SEC)].

In Bezug auf die Polymervorstufe PV schließt sich die vorliegende Erfindung an die Lehre des Standes der Technik (z.B. DE-PS 24 49 656, EP-PS 0 214 551 oder EP-PS 0 218 866) an, wobei die flüssigen Polymervorstufen eine Viskosität von weniger als 5 Pa·s, vorzugsweise von weniger als 0,5 Pa·s bei der zur Formgebung vorgesehenen Temperatur aufweisen.

Als Füllstoffe FS eignen sich die einschlägig für Gießharze verwendeten feinteiligen anorganischen oder organischen Materialien. Die Partikel können farblos oder eingefärbt sein. Zweckmäßig wird eine Korngröße von 200 µm Durchmesser, vorzugsweise 60 µm nicht überschritten. Daneben können aber für spezielle Zwecke noch anders dimensionierte, beispielsweise größere Füllstoffpartikel zur Anwendung kommen, z.B. in Mengen bis ca. 10 Gew.-% bezogen auf die Suspension SP. Bei Anwendung von Cristobalit als Filler sollen vorzugsweise mindestens 95 % der Teilchen < 10 µm groß sein. Teilchen mit einer Größe von $\leq 0,1$ µm sollten nach Möglichkeit nicht mehr als 10 % der gesamten Teilchenzahl ausmachen. Die Teilchengröße wird gemäß den üblichen Verfahren bestimmt (vgl. B. Scarlett in "Filtration & Separation", pg. 215, 1965). Zur Teilchengrößenbestimmung werden die jeweils größten Abmessungen der Partikel herangezogen. Bevorzugt werden kornförmige Partikel. Gelegentlich kann es vorteilhaft sein, die Partikel durch Erhitzen, etwa auf 150 Grad C, von adsorptiv gebundener Feuchtigkeit zu befreien. Die Füllstoffe FS können Naturprodukte oder synthetisch hergestellt sein. Die mechanischen Eigenschaften wie Härte, elastischer Schermodul, bemessen sich nach dem vorgesehenen Anwendungszweck der Gießharze. Dabei kann die Einstel-

lung eines elastischen Schermoduls von wenigstens 5 GNm⁻² vorteilhaft sein. Geeignet sind z.B. Mineralien wie Aluminiumoxide, Aluminiumhydroxide bzw. -oxidhydrate und Derivate, z.B. Alkali- und Erdalkalidoppeloxide und Erdalkalihydroxide, Tone, Siliciumdioxid in seinen verschiedenen Modifikationen, Silikate, Aluminosilikate, Carbonate, Phosphate, Sulfate, Sulfide, Oxide, Kohle, Metalle und Metalllegierungen vorzugsweise in Plättchen- bzw. Flitterform.

Ferner sind synthetische Materialien wie Glasmehl, Keramik, Porzellan, Schlacke, feinverteiltes synthetisches SiO₂ geeignet. Genannt seien Kieselsäuremodifikationen wie Quarz (Quarzmehl) Tridymit und Cristobalit, sowie Kaolin, Talcum, Glimmer, Feldspat, Apatit, Baryte, Gips, Kreide, Kalkstein, Dolomit. Gegebenenfalls können auch Gemische von Füllstoffen angewendet werden. Der Füllstoffanteil an der (füllstoffhaltigen) Suspension SP beträgt vorzugsweise mindestens 40 Gew.-%. Im allgemeinen wird ein Anteil von 80 Gew.-% nicht überschritten. Als Richtwert sei ein Füllstoffgehalt der Suspension SP von > 50 und bis 80 Gew.-% angegeben. Die Herstellung der Füllstoffe in den zweckmäßigen Korngrößen kann nach den bekannten Verfahren erfolgen, z.B. durch Brechen und Mahlen. Besonders bevorzugt ist Cristobalit neben Aluminiumhydroxid. Bevorzugt ist der anorganische Füllstoff so beschaffen, daß das ausgehärtete Gießharz einen elastischen Schermodul von wenigstens 5 GNm⁻², bevorzugt von wenigstens 10 GNm⁻² aufweist, wobei bei der Einstellung der mechanischen Eigenschaften die vorgesehene Anwendung der Gießharze im Auge zu behalten ist.

Bei einer bevorzugten Ausführungsart liegt die durchschnittliche Teilchengröße im Bereich 80 - 0,5 µm, vorzugsweise liegt die Härte (nach Mohs: vgl. Römpp's Chemie-Lexikon, 9. Auflage, S. 1700, Georg Thieme Verlag 1990) der Füllstoffe FS im Falle des Cristobalits bei ≥ 6 , im Falle des Aluminiumhydroxids bei 2,5 - 3,5. Die Silanisierungsmittel Si-M dienen in an sich bekannter Weise als Haftvermittler zwischen Füllstoff und organischer Phase. Es können somit die aus dem Stand der Technik bekannten Organosilicium-Verbindungen eingesetzt werden [vgl. D. Skudelny Kunststoffe 77, 1153 - 1156 (1987); Kunststoffe 68 (1978); Firmenschrift Dynasilan ®, Haftvermittler der Dynamit Nobel Chemie].

In erster Linie handelt es sich um funktionelle Organosiliciumverbindungen mit mindestens einer ethylenisch ungesättigten Gruppe im Molekül. Der die ethylenisch ungesättigte Gruppe tragende funktionelle Rest ist im allgemeinen über ein C-Atom mit dem zentralen Siliciumatom verknüpft. Die verbleibenden Liganden am Silicium sind in der Regel Alkoxyreste mit 1 bis 6 Kohlenstoffatomen (wobei sich noch Etherbrücken im Alkylrest befinden kön-

Temperatur durchgeführt werden, beispielsweise zwischen 50 und 100 Grad C, wobei als Ausgangswert etwa 75 Grad C gelten kann. Die Temperaturführung hat auch hier der entstehenden Polymerisationswärme Rechnung zu tragen. Für den Abschluß des Polymerisationsvorgangs ist das Abklingen der exothermen Reaktion, d.h. das Fallen der Temperatur nach Erreichen eines Temperaturmaximums ein Indikator. Zweckmäßigerweise wird noch über einen gewissen Zeitraum, etwa im Bereich des erreichten Temperaturmaximums nacherhitzt. Anstelle von Polymerisat-Partien können auch anders erzeugte Polymer-Partikel im Teilchengrößenbereich 5 bis 1000 um zur Anwendung kommen. Die Teilchengröße wird nach den üblichen Verfahren bestimmt, wobei zur Bestimmung die jeweils größten Abmessungen der Teilchen herangezogen werden (vgl. B. Scarlett, Filtration & Suspension, S. 215, 1965). So kann z.B. aus festem Polymerisat, z.B. aus Platten durch Zerkleinerung insbesondere Mahlung bis zum erwünschten Feinheitsgrad ein teilchenförmiges Polymermaterial PP gewonnen werden, das den Anforderungen entspricht (vgl. H. Rumpf, Kunststoffe 44, 43,93 (1954); H. Balzer, Polymere Werkstoffe Bd. II, Technologie 1, 105 - 111, Georg Thieme-Verlag 1984). Bewährt hat sich beispielsweise die Mahlung mit einer Schlagkreuzmühle. In an sich üblicher Weise können die Kornfraktionen abgetrennt werden, beispielsweise durch Siebung (vgl. Kirk-Othmer, Encyclopedia of Chemical Technology 3rd. Ed. Vol. 21, pg. 114, J. Wiley 1983). Die Einarbeitung und Verteilung der teilchenförmigen Polymerisate PP in der Suspension SP geschieht zweckmäßig durch Rühren, beispielsweise mittels eines Rühraggregats im allgemeinen im Bereich von 300 - 1000 Upm.

Außer den genannten Komponenten können der Suspension SP noch an sich übliche Hilfsstoffe wie Stabilisatoren, UV-Schutzmittel, Trennmittel, Gleitmittel u.ä. und insbesondere Farbstoffe wie einschlägig verwendete Farbstoffe und Pigmente in Konzentrationen bis etwa 10 Vol.-% in den dafür üblichen Mengen zugesetzt werden (vgl. Ullmann's Encyclopedia of Industrial Chemistry 5th. Ed. Vol. 20A, pg. 459 - 507 VCH 1992). Besonders genannt seien als Farbstoffe Gelb- bzw. Rotpigmente, z.B. solche auf Eisenoxiddbasis, Weißpigmente wie z.B. Titandioxid, Zinksulfid, Schwarzpigmente wie z.B. Schwarzeisen, als Blau- bzw. Grünpigmente solche auf Ultramarin- bzw. Cobalt-Basis. (Vgl. M. & O. Lückert, Pigment- und Füllstofftabellen, Laatz 1980; H. Balzer, Polymere Werkstoffe Bd. II, S. 37 - 353, Georg Thieme-Verlag 1984). Außer Farbstoffen und Pigmenten eignen sich noch andere, an sich bekannte Zusätze, z.B. Metalle und -derivate in verschiedenen Formen, insbesondere in Plättchen- bzw. Flockenform oder als Fasern, Schnitzel, Späne oder Stäube, z.B. aus Aluminium, Kupfer,

Bronze, Silber, Gold, Messing, Chrom, Nickel, Eisen bzw. Stahl, Zinn, Titan, Wolfram, Zink, daneben nicht-metallische Schnitzel oder Flocken z.B. aus Titanitrid, Nickelsulfid, Magnesiumsulfid. Weiter natürliche oder synthetisch gewonnene Flocken, Faserabschnitte u.ä. aus Nylon bzw. Polyamid, Baumwolle, Flachs, Polyester, Glas, Haare, Wolle, Hanf, Papiermasse, Polyacrylnitril, Polyethylen, Polypropylen, Proteine verschiedener Typen, Steinwolle, Holzfasern.

In einer bevorzugten Ausführungsart erfolgt der Zusatz der Farbstoffe als Bestandteil von - gegebenenfalls gefüllten-Polymerpartikeln der oben geschilderten Zusammensetzung. Vorteilhafterweise liegen dabei die durchschnittlichen Teilchengrößen im Bereich 0,01 - 2 mm. Bei zweckmäßiger Verwendung von Pigmenten, z.B. Rot-, Gelb- und/oder Schwarzpigmenten u. ggfs. Weißpigmenten und/oder von metallischen Pigmenten läßt sich z.B. ein Steindekor der Formkörper (Typ: Granit oder Marmor) erzielen.

Durchführung des Verfahrens

Zweckmäßigerweise geht man bei dem erfindungsgemäßen Verfahren von der an sich üblichen Polymervorstufe PV aus, welche Methylmethacrylat und gegebenenfalls die weiteren Monomeren sowie vorzugsweise das Praepolymerisat PM enthält. Weiter enthält die so gebildete, flüssige Phase zweckmäßig die Silanisierungsmittel SHM.

In diese flüssige organische Phase wird nun unter mechanischem Rühren, beispielsweise mittels eines Dissolvers der anorganische Füllstoff FS unter Bildung einer Suspension eingetragen. Als Richtwert für diesen Vorgang seien etwa 10 Minuten genannt. Im allgemeinen erfolgt die Zugabe der Füllstoffe FS derart, daß die Viskosität der organischen Phase nicht über einen Wert von etwa 10 Pa s ansteigt.

Alternativ zur Silanisierung in der organischen Phase kann die Suspension auch mit bereits silanisiertem Füllstoff FS erzeugt werden. Anschließend löst man die Polymerisationshilfsmittel, wie die an sich bekannten Polymerisationsinitiatoren in Mengen von gewöhnlich 0,1 bis 5 Gew.-% bezogen auf die Monomeren M.

Als Polymerisationsinitiatoren werden Radikalbildner eingesetzt, deren Zerfall in Radikale thermisch induziert werden kann. Grundsätzlich sind alle diejenigen geeignet, die bereits bei tiefen Temperaturen einen hohen Radikalstrom liefern (vgl. J. Brandrup, E.H. Immergut, "Polymer Handbook" 3rd. Ed., Kapitel III, Seiten 1 bis 65, J. Wiley, 1989). Genannt seien z.B. Initiatoren, die bei Temperaturen von 40 - 100 Grad C eine Halbwertszeit von 1 Stunde besitzen, wie z.B. tert-Butylperpivalat und Bis-(4-tert-butylcyclohexyl)peroxydicarbonat.

vorstufe PV herstellt, in die unter hochtourigem Rühren unter Bildung einer Suspension SP der partikelförmige Füllstoff FS in Anteilen von 30 bis 80 Gew.-% bezogen auf die gebildete Suspension SP eingetragen wird und wobei man der Suspension SP kurz vor dem Verfüllen in die Polymerisationskammer einen Radikal-Initiator und ein festes, teilchenförmiges Polymerisat PP in Anteilen von 1 bis 20 Gew.-% bezogen auf die Suspension SP in gleichmäßiger Verteilung zusetzt, anschließend in die Polymerisationskammer verfüllt, dann die Polymerisation durchführt und Entformung vornimmt.

2. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß das feste, teilchenförmige Polymerisat PP ein Acrylharz ist.
3. Verfahren gemäß den Ansprüchen 1 und 2, dadurch gekennzeichnet, daß das feste, teilchenförmige Polymerisat PP Füllstoffe und/oder Farbmittel enthält.
4. Verfahren gemäß den Ansprüchen 1 bis 3, dadurch gekennzeichnet, daß das feste, teilchenförmige Polymerisat PP einen Durchmesser im Bereich 5 - 1 000 μm besitzt.
5. Verfahren gemäß den Ansprüchen 1 bis 4, dadurch gekennzeichnet, daß das feste, teilchenförmige Polymerisat PP ein Perlpolymerisat darstellt.
6. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß der partikelförmige Füllstoff FS eine durchschnittliche Teilchengröße im Bereich 60 - 0,5 μm besitzt.
7. Verfahren gemäß den Ansprüchen 1 und 6, dadurch gekennzeichnet, daß der partikelförmige Füllstoff FS anorganisch ist.
8. Verfahren gemäß Anspruch 7, dadurch gekennzeichnet, daß der anorganische Füllstoff FS ein Aluminiumhydroxid ist.
9. Verfahren gemäß den Ansprüchen 1 - 8, dadurch gekennzeichnet, daß den Formteilen Farbmittel zugesetzt werden.
10. Verfahren gemäß Anspruch 9, dadurch gekennzeichnet, daß die Farbmittel in Form von farbigen, gegebenenfalls ebenfalls gefüllten Polymerpartikeln im Teilchengrößenbereich 0,01 - 2 mm zugesetzt werden.

11. Verfahren gemäß den Ansprüchen 1 - 8, dadurch gekennzeichnet, daß die Farbmittel in Form von plättchenförmigen Pigmenten zugesetzt werden.

12. Verfahren gemäß den Ansprüchen 1 - 11, dadurch gekennzeichnet, daß als Formteile Platten hergestellt werden.

13. Verfahren gemäß den Ansprüchen 1 - 11, dadurch gekennzeichnet, daß als Formteile nicht-plane Objekte ausgewählt aus der Gruppe der Spülen, Waschbecken, Bäder- und Duschwannen und sonstigen Sanitärartikel hergestellt werden.

E4

(19) European Patent Office

(11) Publication No.: **0639539 A1**

(12)

EUROPEAN PATENT APPLICATION

(21) Application No.: **94112189.9**

(51) Int. Cl.⁶: **C04B 26/06, C08F 2/44,
C08K 3/22, C08K 3/00,
A47K 1/00, A47K 3/00**

(22) Filing date: **4.8.94**

(30) Priority: **17.8.93 DE 4327610**

(71) Applicant: **RÖHM GMBH
Kirschenallee
D-64293 Darmstadt (DE)**

(43) Date of publication of the application:
22.2.95 Patentblatt 95/08

(72) Inventor: **Dr. Manfred Krieg
Kesselhutweg 19
D-64289 Darmstadt (DE)
Inventor: Günther Ittmann
Waldstrasse 15
D-64823 Gross-Umstadt (DE)**

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB IT LI NL SE

(54) Process for the manufacture of cast, highly-filled polymethyl methacrylate mouldings.

(57) The invention relates to a process for the manufacture of filled mouldings based on polymethyl methacrylate by substance polymerization in a suitable polymerization chamber, wherein in a manner known in itself, a liquid polymer pre-stage PV containing the monomers is produced, into which the particulate filler material FS is fed with high-speed stirring to form a suspension SP, the filler material FS being added in amounts of 30 to 80 wt% of the suspension SP so formed, and wherein a radical initiator and a solid particulate polymer PP are added, with uniform dispersion, to the suspension SP shortly before it is filled into the polymerization chamber, the polymer PP being added in amounts of 1 to 20 wt% of the suspension SP, which is then filled into the polymerization chamber, after which polymerization is effected and the product is removed from the mould.

Subject-matter of the invention

The invention relates to a process for the manufacture of cast, highly-filled PMMA mouldings.

State of the art

Transparent polymethyl methacrylate panels, so-called "cast PMMA panels", are traditionally produced by substance polymerization methods (cf. H. Rauch-Puntigam, Th. Völker, *Acryl- und Methacrylverbindungen* [Acrylic and methacrylic compounds], Springer-Verlag 1967, pp. 275-292). In addition to the transparent "acrylic glasses", acrylic resins doped with fillers, chiefly of an inorganic nature, have gained in importance, particularly in sanitary and kitchen ware and as decorative panels, etc. Thus, DE-A 3528165 describes plastic elements made cloudy with crosslinked beads. DE-A 4216341 proposes light-diffusing PMMA mouldings obtained by the addition of *inter alia* crosslinked particles containing phenyl groups. Again, a process for the manufacture of acrylate plastics with a colour-differentiated surface using coloured polymer beads is described in DE-A 3110093. Electrically conducting plastics have also been described whose conductivity relies on the presence of polymer particles superficially provided with conductive materials (DE-A 3543301). In principle, the technology that has been tried and tested for the manufacture of transparent PMMA panels seems applicable to the manufacture of panels doped with filler material, including so-called "highly-filled" panels.

In US-A 3706825, for example, a continuous process using extruders for the manufacture of highly-filled imitation marbles is described.

Problem and solution

Problems which have to be solved in the manufacture of cast, filled mouldings in general will now be indicated in the context of the manufacture of cast, filled panels.

Hitherto, filled PMMA panels obtained by directly applying the production technique for cast PMMA panels have not been satisfactory. The industry often uses redox systems as initiators (cf. Rauch-Puntigam *et al.*, *loc. cit.*) with a view to speeding up the polymerization process. Numerous problems are encountered when this method is applied to the manufacture of highly-doped panels. Thus, when producing thick panels (e.g. 10 - 20 mm thick) with large dimensions, onset of polymerization is observed while filling [into the moulding chamber] is still taking place, so that controlled polymerization in the cars normally used is quite impossible. Furthermore, the uncontrolled polymerization process causes panel stresses leading to stress cracking.

With "slow" polymerization (say 2 - 3 hours in the water bath), there is such heavy sedimentation of the relatively coarse filler-particles that the panels obtained are inhomogeneous and are distinctly warped. Nor can this sedimentation be entirely suppressed by the use of syrup containing the polymer.

So, although "slow" polymerization has suggested itself in principle, this approach has been put off by the side effects, in particular the sedimentation accompanied by warping of the panels which has been seen as inevitable.

The problem has therefore existed of making available a process for the manufacture of filled PMMA mouldings with which the deficiencies which have been described can be overcome while preserving the same basic requirements in terms of apparatus.

This problem is solved in a most satisfactory manner by the process according to the invention.

The invention, then, relates to a process for the manufacture of filled mouldings based on polymethyl methacrylate by substance polymerization in a suitable polymerization chamber, wherein in a manner known in itself a liquid polymer pre-stage PV containing the monomers is produced, into which the particulate inorganic filler material FS is fed with high-speed stirring to form a suspension SP, the filler material FS being added in amounts of 30 - 80 wt% of the suspension SP so formed, and wherein a radical initiator or an initiator system [and] a solid particulate polymer PP, preferably also based on PMMA, are added with uniform dispersion to the suspension SP prepared for

polymerization shortly before it is filled into the polymerization chamber, the polymer PP being added in amounts of 1 to 20 parts by weight of the suspension SP.

At least 50 and up to 100 wt% of the monomers of the pre-stage PV consists of methyl methacrylate, possibly with other alkyl esters or aryl esters of (meth)acrylic acid with usually 1 - 8 carbon atoms appropriately used as copolymers, such as e.g. ethyl(meth)acrylate, propyl(meth)acrylate, butyl(meth)acrylate and/or isomers, 2-ethylhexyl(meth)acrylate, cyclohexyl(meth)acrylate, phenyl(meth)acrylate, [and] benzyl(meth)acrylate. The polymer pre-stages may additionally contain crosslinking monomers known in themselves, for example those with at least two polymerizable vinyl groups in the molecule (cf. H. Rauch-Puntigam, Th. Völker, *Acryl- und Methacrylverbindungen*, Springer-Verlag, 1967, p. 184), of which ethyleneglycoldimethacrylate, 1,4-butanedioldimethacrylate, triglycoldimethacrylate, trimethylolpropanetrimethacrylate and -acrylate, [and] allyl compounds such as allylmethacrylate or triallylcyanurate, may be cited as examples. The crosslinking monomer content is generally around 0.1 to 1.5 wt% of the monomers. In addition to the monomers, the polymer pre-stage PV preferably contains a pre-polymer PM in amounts of 1 to 15 wt% of the polymer pre-stage PV.

Examples of possible pre-polymers PM are appropriate PMMA polymers, which may optionally contain minor amounts of up to say 15 wt% of judiciously selected comonomers such as e.g. methyl acrylate. The pre-polymers normally have a molar mass in the range 2×10^4 to 4×10^5 (determination by size exclusion chromatography (SEC)).

With regard to the polymer pre-stage PV, the present invention follows the teaching of the prior art (e.g. DE-PS 2449656, EP-PS 0214551 or EP-PS 0218866) in that the liquid polymer pre-stages have a viscosity of less than 5 Pa.s, preferably less than 0.5 Pa.s, at the intended moulding temperature.

Suitable for use as filler materials FS are the finely divided inorganic or organic materials appropriately used for casting resins. The particles may be colourless or colour-imbued. It is expedient not to exceed a grain size of 200 μm diameter, and preferably 60 μm . However, filler particles in other sizes, for example larger filler particles, may additionally

be used for special purposes, e.g. in amounts of up to approx. 10 wt% of the suspension SP. Where cristobalite is used as filler, at least 95% of the particles should preferably be less than 10 μm . So far as possible, particles with a size of 0.1 μm or less should not make up more than 10% of the total number of particles. The particle size is determined by the usual methods (cf. B. Scarlett in "Filtration & Separation", p. 215, 1965). In each case, it is the largest dimensions of particles that form the basis of the particle size determination. Granular particles are preferred. Sometimes it may be advantageous to rid the particles of adsorptively acquired moisture by heating, say to 150 degrees C. The filler materials FS may be natural products or artificially produced. Their mechanical properties such as hardness and elastic shear modulus will be governed by the intended application of the casting resins. It may be advantageous to set an elastic shear modulus of at least 5 GNm^{-2} . Examples of suitable materials are minerals such as aluminium oxides [and] aluminium hydroxides or oxide hydrates, and derivatives, e.g. alkaline and alkaline-earth double oxides and alkaline-earth hydroxides, clays, silicon dioxide in its various modifications, silicates, aluminosilicates, carbonates, phosphates, sulphates, sulphides, oxides, coal, metals and metal alloys, preferably in lamina or flake form.

Synthetic materials such as glass powder, ceramics, porcelain, slag, [and] finely dispersed synthetic silicon dioxide, are also suitable. Worthy of mention are silicic acid modifications such as quartz (quartz powder) tridymite and cristobalite, and also china clay, talc, mica, feldspar, apatite, barite, gypsum, chalk, limestone, [and] dolomite. Also, mixtures of filler materials may optionally be used. The filler content of the suspension SP (including filler) is preferably at least 40 wt%. Generally it will not exceed 80 wt%. A filler content in the suspension SP of more than 50 and up to 80 wt% may be quoted as a guide. Fillers in appropriate grain sizes can be produced by known methods, e.g. by crushing and grinding. Besides aluminium hydroxide, cristobalite is especially preferred. Preferably, the constitution of the inorganic filler is such that the cured casting resin will have an elastic shear modulus of at least 5 GNm^{-2} and preferably at least 10 GNm^{-2} ; the intended application of the casting resins should be borne in mind when setting the mechanical properties.

In one preferred way of carrying out the invention, the average particle size lies in the range 60 - 0.5 μm , while the hardness (according to Mohs: cf. *Römp's Chemie-Lexikon*,

9th Edition, p. 1700, Georg Thieme Verlag 1990) of the filler materials FS is preferably about 6 or higher in the case of cristobalite and about 2.5 - 3.5 in the case of aluminium hydroxide. The silanizing agents Si-M act, in a manner known in itself, as promoters of the bond between filler and organic phase. Hence the organo-silicon compounds known from the state of the art can be used (cf. D. Skudelny, *Kunststoffe* 77, 1153-1156 (1987); *Kunststoffe* 68 (1978); Company publication Dynasilan®, bond promoter, Dynamit Nobel Chemie).

Of primary interest are functional organo-silicon compounds with at least one ethylenically unsaturated group in the molecule. The functional radical carrying the ethylenically unsaturated group is generally linked to the central silicon atom by a carbon atom. The remaining ligands on the silicon are usually alkoxy radicals with 1 to 6 carbon atoms (with the possibility of the presence of ether crosslinks in the alkyl radical). Examples are the vinyltrialkoxysilanes. The CC double bond may also be linked by one or more carbon atoms to the silicon atom, e.g. in the form of the allyltrialkoxysilanes or the γ -methacryloyloxypropyltrialkoxysilanes. Dialkoxysilanes may also be used, in which case a further functional radical with the CC double bond, mostly of the same type, or an alkyl radical preferably with 1 to 6 carbon atoms, is linked to the silicon atom. Various types of organo-silicon compounds may also be present in the organo-silicon component. Examples of such compounds are vinyltrimethoxysilane, vinyltriethoxysilane, vinyltris(methoxyethoxy)silane, divinyl dimethoxysilane, vinylmethyldimethoxysilane, vinyltrichlorosilane, γ -methacryloyloxypropyltrimethoxysilane or γ -methacryloyloxypropyltris(methoxyethoxy)silane. The organo-silicon compounds are advantageously used with catalysts of the amine type, particularly of the alkyl amines type, with 3 to 6 carbon atoms, especially with n-butylamine. Guide values of 0.05 to 10 wt%, preferably 1 to 5 wt%, of the organo-silicon component may be assumed for the use of the amine catalyst.

In general the weight ratio of inorganic filler materials to organo-silicon compound is 500:1 to 20:1, preferably 50 \pm 25:1. It is crucially important to the process according to the invention that the solid particulate polymer PP be added to the formed suspension SP prepared for polymerization.

The particulate polymer PP is, advantageously, also an acrylic resin, in particular PMMA or an MMA copolymer, for example with the monomers suggested for the polymer pre-stage PV (see above) and/or other suitable vinylic monomers, usually in amounts not exceeding 20 wt% of the polymer PP, in particular in amounts of 0.2 - 15 wt% (cf. *Ullmanns Enzyklopädie der Technischen Chemie*, 3rd Ed., Vol. 14, pages 108 to 110, Urban & Schwarzenberg, 1963), e.g. vinyl esters and ethers, and also vinyl compounds, vinylic carbon compounds, vinyl aromatics, heterocyclic vinyl compounds and others. The polymers which form the PP particles generally have a molecular weight, in the non-crosslinked condition, ranging from 10,000 to 2,000,000 dalton.

Optionally the polymers may also contain crosslinking monomers as reported for the polymer pre-stage PV, i.e. the beads may be crosslinked. The polymer particles PP usually have a diameter in the 5 to 1000 μm range. Most especially preferred are polymers PP in bead form, particularly in an average particle-size range of 0.02 to 0.3 mm, especially in the range 0.03 - 0.15 mm. The production of polymer beads of a suitable type is described for example in DE-A 3130093, DE-A 2135828 and DE-A 2815506. The PP beads may themselves be doped with fillers and/or pigments, the doping generally being similar in quality and quantity to that described for the suspension SP. The polymerization of the beads is based in a known manner on reaction of monomers with low solubility in water (or salting-out effect) in water or aqueous salt solution. Besides accelerators and appropriate polymerization-promoters, suspension stabilizers, e.g. water-soluble protective colloids, are used. The size of the beads is essentially controlled, in a known manner, by the technical process conditions, e.g. the rate of stirring and the nature and quantity of suspension stabilizers. Monomer-soluble, water-insoluble radical-initiators, e.g. dibenzoyl peroxide and lauroyl peroxide, besides azoinitiators, are generally used. High disintegrators [*Hochzerfaller*] may optionally be added towards the end of the polymerization process (cf. Brandrup-Immergut, *Polymer Handbook*, 3rd ed., Chapter III, pp. 1-65, J. Wiley 1989). As a rule the proportion to the monomers is 0.1 to 1 wt%, preferably around 0.5 wt%.

As regulators — as in the substance polymerization starting from the polymer pre-stage PV — the usual sulphur regulators are used. Aliphatic mercaptans and/or sulphur ethers have proved particularly useful. Possible examples include laurylmercaptan, bis-(2-ethylhexyl)sulphide, bis-(2-mercaptoethyl)sulphide, and similar. The amount of

regulators is generally 0.01 to 1.0 wt%, preferably 0.05 to 0.4 wt%, of the monomers. The molar weight (M_w) of the beads to be used in accordance with the invention generally lies between 10^4 and 2×10^6 , preferably between 10^5 and 10^6 (determination by gel permeation chromatography; cf. H. F. Mark *et al.*, Encyclopedia of Polymer Science & Technology, Vol. 10, pp. 1-19, J. Wiley 1987). Unregulated or weakly crosslinked beads may also be used if required.

As suspension stabilizers, macromolecular water-soluble compounds such as e.g. polyvinyl alcohol or polyacrylic acid in an amount of 0.01 to 1 wt% of the monomers, may be used; or inorganic powder additives may be added as such or produced through precipitation in the medium. Possible examples include alkaline-earth salts such as carbonates, sulphates, silicates etc. (cf. C. E. Schildknecht, Polymerization Processes, J. Wiley & Sons 1977, pp. 119 ff.). The bead polymerization may be performed at increased temperature, for example at between 50 and 100 degrees C. An initial value of around 75 degrees C may be adopted. The temperature management has to take account of the heat of polymerization evolved. The dying-away of the exothermic reaction, that is to say the fall in temperature after a maximum temperature has been reached, is an indicator of the completion of the polymerization process. It is advisable to continue heating for a certain period, approximately in the range of the maximum temperature attained.

Polymer particles in a particle-size range of 5 to 1000 μm that have been produced in other forms may be used instead of polymer beads.

The particle size is determined by the usual methods, and is based on the largest dimensions of the particles (cf. B. Scarlett, Filtration & Suspension, p. 215, 1965). A particulate polymer material PP that meets the requirements can be obtained e.g. from solid polymer, e.g. from a sheet or slab, by pulverizing, in particular by grinding, down to the required fineness (cf. H. Rumpf, *Kunststoffe* 44, 43,93 (1954); H. Balzer, *Polymere Werkstoffe* Vol. II, *Technologie* 1, 105-111, Georg Thieme-Verlag 1984). For instance, grinding with a hammer bar mill has proved effective. The grain fractions may be separated in a manner known in itself, e.g. by screening (cf. Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd Ed., Vol. 21, p. 114, J. Wiley 1983). The particulate

polymers PP are expediently incorporated and dispersed in the suspension SP by stirring, for example with an apparatus generally operating in the 300 - 1000 rpm range.

Apart from the components which have been mentioned, customary additives such as stabilizers, UV protection agents, parting agents, lubricants and the like, and, in particular, colouring agents such as appropriately used dyes and pigments in concentrations of up to about 10% vol., may be added to the suspension SP in the usual amounts (cf. Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed., Vol. 20A, pp. 459-507, VCH 1992). Especially worthy of mention among possible colouring agents are yellow and red pigments such as those based on iron oxide, white pigments such as titanium dioxide, zinc sulphide, black pigments such as carbon blacks, and ultramarine- and cobalt-based blue and green pigments. (Cf. M. & O. Lückert, *Pigment- und Füllstofftabellen*, Laatzten 1980; H. Balzer, *Polymere Werkstoffe* Vol. II, pp. 37-353, Georg Thieme-Verlag 1984). Besides dyes and pigments, other additives known in themselves are also suitable: e.g. metals and metal derivatives in various forms, particularly in lamina or flake form or as fibres, chips, swarf or dust e.g. of aluminium, copper, bronze, silver, gold, brass, chromium, nickel, iron and steel, tin, titanium, tungsten, [or] zinc, and also non-metallic chips or flakes e.g. of titanium nitride, nickel sulphide [or] magnesium sulphide. Also natural or artificially obtained flocks, chopped fibres, and the like, of nylon or polyamide, cotton, flax, polyester, glass, hair, wool, hemp, paper pulp, polyacrylonitrile, polyethylene, polypropylene, proteins of various types, mineral wool, [or] wood fibre.

In a preferred way of carrying out invention, the colouring agents are added as a constituent of (possibly filled) polymer particles with the composition described above. Advantageously, the average particle sizes lie in the 0.01 - 2 mm range. With judicious use of pigments, e.g. red, yellow and/or black pigments and possibly white pigments, and/or of metallic pigments, e.g. a (granite or marble type) stone effect can be obtained in the mouldings produced.

Execution of the process

It is expedient to carry out the process according to the invention by starting from the polymer pre-stage PV, usual in itself, containing methyl methacrylate and optionally the

other monomers and preferably the pre-polymer PM. The liquid phase thus formed also conveniently contains the silanizing agent Si-M.

The inorganic filler material FS is then fed into this liquid organic phase with mechanical stirring, for example with a dissolver, so forming a suspension. As a guide, this step may last about 10 minutes. Usually the fillers FS are added in such a way that the viscosity of the organic phase does not rise above a value of about 10 Pa.s.


As an alternative to silanization in the organic phase, the suspension can also be produced with ready-silanized filler FS.

The polymerization promoters such as polymerization initiators known in themselves are then dissolved, usually in amounts of 0.1 to 5 wt% of the monomers M.

Radical-formers whose breakdown into radicals can be thermally induced are used as polymerization initiators. In principle, all those which already deliver a high flow of radicals at low temperatures are suitable (cf. J. Brandrup, E. H. Immergut, "Polymer Handbook", 3rd Ed., Chapter III, pages 1 to 65, J. Wiley, 1989). Particularly suitable are initiators possessing a half-life period of 1 hour at temperatures of 40 - 100 degrees C, such as e.g. tert.-butylperpivalate and bis-(4-tert.-butylcyclohexyl)peroxydicarbonate.

It is advisable not to add the initiators until shortly before the casting resin suspensions are filled [into the moulding chambers]. The particulate polymers PP are then added, likewise shortly before filling into the moulding chambers, and if possible before any significant swelling of the polymers PP has taken place. The feeding of the particulate polymers PP into the suspension may advantageously be performed by means of a mixing extruder with vacuum degassing or with a twin-screw extruder. Advantageously, the suspension is evacuated before filling [into the moulding chamber].

The swelling of the polymers PP in the polymerization chamber raises the viscosity, or structural viscosity, sufficiently to permit, at most, only an innocuous amount of further sedimentation of filler material.

The time to the onset of swelling or to the rise in viscosity, and the magnitude of the rise in viscosity, can be controlled through the molecular weight, particle size and amount of the polymer PP. 

The rapid gelling of the suspension means that the filled polymerization chambers can be left standing for an extended period (say $\frac{1}{2}$ - 1 hour) with no sedimentation. This makes it possible for larger units, e.g. whole cars, to undergo polymerization at a time.

The actual curing (= polymerization) preferably takes place with an input of thermal energy, for example in a water bath by heating to 35 - 80 degrees C, for example for 20 to 300 minutes, either with or without application of pressure. The mouldings, e.g. polymer panels, are then stripped from the mould in a manner known in itself. The residual monomer contents of the cured polymers are usually below 1 wt%, in particular below 0.5 wt%, of the total monomers.

Advantageous effects

Surprisingly, the process according to the invention allows even large, and relatively thick, filled PMMA panels, in dimensions of say 4000 x 2500 x 20 mm, to be manufactured with state-of-the-art equipment.

Because the polymerization can be carried out reproducibly under defined conditions, the consequences of uncontrolled polymerization such as e.g. stresses in the product can be avoided.

Owing to the absence of filler sedimentation, there are no warped, inhomogeneous panels. As has been stated, the process offers a number of ways of controlling the magnitude and timing of the rise in viscosity.

Also, the possibility of using standard equipment to manufacture cast PMMA panels appears especially attractive.

Furthermore, the process is also suitable for the manufacture of three-dimensional shapes such as e.g. sinks, washbasins, bath and shower tubs and other sanitary ware.

|| A decorative stone effect can be obtained in all applications through suitable colouring. //

The possibility of carrying out the process according to the invention as a continuous process should also be emphasized.

EXAMPLES

Example 1

Into a syrup consisting of 9.569 kg of methyl methacrylate, 950 g of a polymethyl methacrylate with a molar mass M_w of approx. 3×10^5 g/mol (PLEXIGUM® M 920 of Röhm GmbH), 1.14 g of 2,4-dimethyl-6-tert.-butylphenol, 114 g of glycoldimethacrylate, 190 g of stearic acid and 5.7 g of 1-isopropyl-4-methyl-1,4-cyclohexadiene, 25.270 kg of aluminium hydroxide consisting of a mixture with mean particle sizes of 45 μm and 7 - 8 μm (products ALCOA C33 and ALCOA C333) is introduced and dispersed, with stirring, on a dissolver. Then, 38 g of bis-(4-tert.-butylcyclohexyl)peroxydicarbonate, 38 g of tert.-butylperpivalate and 19 g of tert.-butylperoctoate are dissolved in the suspension. After stirring-in 1900 g of a particulate polymethyl methacrylate with $M_w = \text{approx. } 5 \times 10^5$ g/mol; ave. particle size approx. 50 μm (product PLEXIDON® M727 of Röhm GmbH), the mix is evacuated and filled into a silicate glass chamber spaced at 12 mm. The sealed chamber is kept in a water bath at a temperature of 40 degrees C for 160 minutes. Final polymerization takes place in an oven at 110 degrees C for a period of 60 minutes. After the chamber has cooled, the panel moulding can be removed. The panel is found to be free from bubbles and from warping. ↑

Claims

1. Process for the manufacture of filled mouldings based on polymethyl methacrylate by substance polymerization in a suitable polymerization chamber, characterized in that
in a manner known in itself, a liquid polymer pre-stage PV containing the monomers is produced, into which the particulate filler material FS is fed with high-speed stirring to form a suspension SP, the filler material FS being added in amounts of 30 to 80 wt% of the suspension SP so formed, and wherein [*sic*] a radical initiator and a solid particulate polymer PP are added, with uniform dispersion, to the suspension SP shortly before it is filled into the polymerization chamber, the polymer PP being added in amounts of 1 to 20 wt% of the suspension SP, which is then filled into the polymerization chamber, after which polymerization is effected, and the product is removed from the mould.
2. Process according to Claim 1, characterized in that the solid particulate polymer PP is an acrylic resin.
3. Process according to Claims 1 and 2, characterized in that the solid particulate polymer PP contains filler materials and/or colouring agents.
4. Process according to Claims 1 to 3, characterized in that the solid particulate polymer PP has a diameter in the range of 5 - 1000 μm .
5. Process according to Claims 1 to 4, characterized in that the solid particulate polymer PP is presented in bead form.
6. Process according to Claim 1, characterized in that the particulate filler material FS has an average particle size in the range of 60 - 0.5 μm .
7. Process according to Claims 1 and 6, characterized in that the particulate filler material FS is inorganic.

8. Process according to Claim 7, characterized in that the inorganic filler material FS is an aluminium hydroxide.
9. Process according to Claims 1 - 8, characterized in that colouring agents are added to the mouldings.
10. Process according to Claim 9, characterized in that the colouring agents are added in the form of coloured, and possibly also filled, polymer particles in the particle size range 0.01 - 2 mm.
11. Process according to Claims 1 - 8, characterized in that the colouring agents are added in the form of laminar pigments.
12. Process according to Claims 1 - 11, characterized in that the mouldings produced are flat panels.
13. Process according to Claims 1 - 11, characterized in that the mouldings produced are three-dimensional shapes selected from the group comprising sinks, washbasins, bath and shower tubs and other sanitary ware.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER: _____**

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.